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(54) Title: PROCESS FOR THE CONVERSION OF HYDROCARBONS  (57) Abstract  A process for the conversion of a hydrocarbon feed in which the feed is contacted with a zeolite catalyst to produce a product, the zeolite having a framework structure which includes a 10- or 12-member channel that is not intersected by another 10- to 12-member channel and having been treated by a process which comprises a first step of contacting the zeolite with steam and a subsequent step of contacting the zeolite with an acid.		

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PROCESS FOR THE CONVERSION OF HYDROCARBONS

This invention relates to a process for the conversion of hydrocarbons using a zeolite catalyst and to a method of regenerating the spent zeolite catalyst.

5 EP-A-247802 discloses that zeolites Theta-1 and ZSM-23 can be used as catalysts in the restructuring of a C<sub>2</sub>-C<sub>10</sub> olefinic feedstock. The feedstock, rich in linear olefins, is converted into a product enriched in branched olefins. Zeolite Theta-1 is also known as Nu-10, ZSM-22, KZ-2 and ISI-1 and its systematic nomenclature is TON.

10 EP-A-65400 discloses that zeolite Nu-10 can be used for the conversion of methanol to olefins, and for alkylation of alkylbenzenes.

Our European UK application No. 913101846 discloses a process for the production of olefins which comprises passing a feedstock  
15 containing C<sub>3</sub> and/or C<sub>4</sub> olefins together with methanol, formaldehyde and/or dimethylether, in a molar ratio greater than 1:20, over a TON-type zeolite.

US Patent No. 4579993 discloses a process for the conversion of methanol to olefins using a zeolite catalyst wherein the catalyst is  
20 treated to both steaming and acid-extraction. The preferred catalyst is ZSM-5.

US Patent No. 4658075 discloses a process for converting aromatic compounds using a crystalline zeolite which has been treated by contact with steam, followed by an aluminium compound  
25 followed by contact with an aqueous acid solution.

We have now found that zeolites which can deactivate rapidly due to their unidimensional structure can be activated using a steam/acid treatment process, and their use in hydrocarbon conversion processes results in surprisingly higher conversion values and little loss in conversion values with time.

Accordingly, the present invention provides a process for the conversion of a hydrocarbon feed characterised in that the feed is contacted with a zeolite catalyst to produce a product, said zeolite having a framework structure which includes a 10- or 12-member channel that is not intersected by another 10- or 12-member channel, and having been treated by a process which comprises a first step of contacting the zeolite with steam and a subsequent step of contacting the zeolite with an acid.

The process of the present invention is suitably directed to the conversion of an olefin containing feed and to the production of a hydrocarbon which is suitably an olefin which is different to that of the feed. The preferred conversion reactions are the conversion of a linear olefin to a branched olefin; the alkylation of aromatics with olefins to produce alkyl benzene; dimerisation and/or oligomerisation of olefins; and the reaction of methanol, formaldehyde and/or dimethyl ether with an olefin to produce higher olefins.

A particularly preferred process is the reaction of C<sub>3</sub> and/or C<sub>4</sub> olefins with methanol, formaldehyde and/or dimethylether, to produce higher olefins. The molar ratio of olefin to methanol, formaldehyde and/or dimethylether is preferably greater than 1 to 20 to 100 to 1, more preferably greater from 1:10 to 10:1, especially from 1 to 1 to 5 to 1. The reaction is preferably carried out at a temperature in excess of 200°C, preferably 250 to 600°C and may be carried out at reduced, atmospheric or elevated pressure. The pressure is the total pressure of the reaction chamber. Suitably, a pressure of from 10-10,000 KPa absolute, preferably 50-1000 KPa absolute may be used. The feedstock may be fed into the reaction chamber either with or without diluents, e.g. water, steam, alkanes or inert gas. The product of the process includes branched olefinic

hydrocarbons, rich in isobutene and methylbutenes. A small amount of by-products, e.g. methane, ethane, ethene and linear olefins are also present.

A further particularly preferred process is the conversion of a C<sub>4</sub>-C<sub>10</sub>, preferably C<sub>4</sub>-C<sub>6</sub>, linear olefin to a branched olefin. The reaction is preferably carried out at a temperature in the range of from 200 to 550°C, especially 300-550°C. The feedstock is preferably diluted with a gas or gases inert under the reaction conditions, for example nitrogen or a C<sub>1</sub>-C<sub>10</sub> alkane. When a diluent is present, it is preferably present in an amount of at least 30% v/v, preferably from 30-80% v/v, of the total mixed feed. The reaction is preferably carried out at a pressure of from 50 to 1000 KPa, especially 100 to 300 KPa.

Zeolites which may be used in the present invention include TON (Theta-1, Nu-10, ZSM-22, KZ-2, ISI-1), MTT (ZSM-23, EU-13, ISI-4, KZ-1), ZSM-48, FER (FU-9, Nu-23, ISI-6, ZSM-35), and EUO (EU-1, TPZ-3, ZSM-50), all of which contain a 10-membered channel that is not intersected by another 10- or 12-membered channel; and MTW (ZSM-12, CZH-5, Theta-3, TPZ-12) and MOR (mordenite), which contain a 12-membered channel that is not intersected by another 10- or 12-membered channel. These structures contrast, for example, with that of MFI (ZSM-5), which contains a 10-membered channel, but in which the channel is intersected by a further 10-membered channel. The use of TON is preferred.

Information on zeolite structures is given in the Atlas of Zeolite Structure Types by Meier W M and Olsen D H, 1992, published by Butterworths, Zeolites vol 2, No.15, June 1992. All of these known zeolite structure types can be prepared by published literature methods. Typical general methods are given, for example, in "Synthesis of High-Silica Aluminosilicate Zeolites" by P A Jacobs and J A Martens, Studies in Surface Science and Catalysis vol. 33, Elsevier, 1987; and "Zeolite Molecular Sieves" by D W Breck, John Wiley, 1974.

A synthetic zeolite immediately after synthesis contains cations which, depending upon the precise synthesis method used,

may be hydrogen, aluminium, alkali metals, organic nitrogen cations or any combination thereof. The zeolite treated by the treatment process may be in the hydrogen form. The hydrogen form may be achieved by, in the case of organic containing zeolite, calcination  
5 to remove the organics followed by either ammonium ion exchange or proton exchange with an acid solution or a combination of both. In the case of a zeolite synthesised in the absence of organic nitrogen containing compounds the hydrogen form could, if desired, be prepared by either direct ammonium ion exchange followed by  
10 calcination or proton exchange with acid solution or a combination of both. If the zeolite to be treated is not in the hydrogen form, the second step of the treatment process, the treatment with acid, will of course introduce protons into the zeolite.

For use as a catalyst, the zeolite may, if desired, be bound in  
15 a suitable binding material. The binder may suitably be one of the conventional alumina, silica, clay or aluminophosphate binders or a combination of binders. The zeolite used in the process of the present invention is treated with a two step treatment process. The treatment process may be applied to the zeolite at any desired point  
20 in the catalyst preparation; it may for example be applied to the zeolite in a powder form, in the form of an extrudate or in a bound form. The treatment method is particularly useful for improving the long-term performance of the catalyst.

Preferably the first step of the zeolite treatment process is  
25 carried out at a temperature in the range of from 100 to 800°C, especially 400 to 600°C. The steam partial pressure may be 100%, or other gases may be present as desired; for example, the steam may be in admixture with a diluent such as nitrogen or air. The total pressure is not crucial; atmospheric pressure is  
30 convenient, but other pressures, for example in the range 10 to 10000 KPa may be used if desired.

The subsequent step of contacting the zeolite with an acid is preferably carried out using a dilute aqueous acid. Acids for use in the treatment of the zeolite may be mineral acids. The preferred  
35 acids are nitric acid, hydrochloric acid or sulphuric acid. The

strength of the acid may be suitably from 0.01 molar, preferably 0.05 to 10 molar. The contact with acid is preferably carried out at a temperature in the range of from 5 to 200°C especially 80 to 120°C, for a period of suitably 0.1 to 10 hours, preferably 0.5 to 2 hours. Following the acid treatment, the zeolite is preferably washed with water, dried and calcined before being used as a catalyst.

According to a further aspect of the invention, there is provided a treatment process for a zeolite which comprises a first step of contacting the zeolite with steam and a subsequent step of contacting the zeolite with an acid wherein said zeolite is selected from the structure types TON, ZSM-48, FER, EUO and MTW.

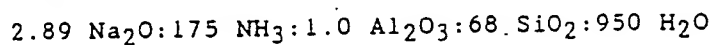
A particular benefit of the present invention is the ability of attaining high initial conversion rates and loss of conversion with time is less rapid than prior art processes.

The following Examples illustrate the invention.

#### Example 1

##### Synthesis of Theta-1 Zeolite

Theta-1 was synthesised using ammonia as the templating agent. Sodium aluminate (30 g, ex.BDH, 40 wt%  $\text{Al}_2\text{O}_3$ , 30 wt%  $\text{Na}_2\text{O}$  and 30 wt%  $\text{H}_2\text{O}$ ) and sodium hydroxide (15.6 g ex.BDH) were dissolved in distilled water (240 g). Ammonia solution (1400 g, SG 0.90 containing 25%  $\text{NH}_3$ ) was added with gentle mixing. 1200 g of silica gel sold under the Trade Mark Ludox AS40 (ex. Du Pont) which contained 40 wt% silica was added over fifteen minutes with stirring to maintain a homogeneous hydrogel. The molar composition of the hydrogel was:-



The mixture was then loaded into a 5 litre Parr autoclave and crystallised at 175°C for 25 hours under autogeneous pressure whilst mixing by a mechanical stirring action. At the end of the crystallisation period the autoclave was cooled, and the product filtered, washed and dried in an air oven at 100°C. The zeolite product was examined by X-ray powder diffraction and found to be highly crystalline Theta-1.

The as made Theta-1 which contained both  $\text{Na}^+$  and  $\text{NH}_4^+$  ions was directly ion exchanged in order to remove the  $\text{Na}^+$  ions by mixing for 1 hour with an aqueous ammonium nitrate solution (1M, zeolite to solution weight ratio of 1:10). The zeolite was filtered, washed and the ion exchange treatment repeated. The ammonium form of the zeolite was then dried at  $100^\circ\text{C}$  and calcined overnight in air at  $550^\circ\text{C}$  to convert it to the hydrogen form. The X-ray diffraction pattern of the zeolite product is shown in Table 1.

TABLE 1: XRD OF PRODUCT OF EXAMPLE 1

2 THETA	D SPACINGS $\text{\AA}$	RELATIVE INTENSITIES $100 \times I/I_{\text{max}}$
8.17	10.81	100
10.16	8.70	22
12.81	6.91	23
16.36	5.42	11
19.42	4.57	12
20.36	4.36	97
24.22	3.67	82
24.64	3.61	52
25.76	3.46	36

Variation in intensities of  $\pm 20\%$ .

Variation in 2 theta positions of  $\pm 0.2^\circ$  with corresponding variation in D spacings.

Peaks below 10% of  $I_{\text{max}}$  excluded.

Copper alpha-1 wavelengths, 1.54060.

X-ray Diffractometer Philips PW 1820/00

Slits  $1/4^\circ$ ,  $0.2^\circ$ ,  $1/4^\circ$

2 Theta Scan  $2^\circ - 32^\circ$

Step Scan  $0.025^\circ$

Time 4 sec



Example 2Catalyst Steaming and Acid Treatment

The H-form of the zeolite as prepared in Example 1 was pressed under 10 tonnes pressure into tablets which were broken into granules and these in turn were sieved to pass 600 micron but not 250 micron sieves. The granules were placed in a tubular reactor (60 mm ID) and heated to 550°C. There was a large preheating zone on which water was converted to steam before it came into contact with the catalyst granules. Distilled water and nitrogen were passed through the preheating zone over the catalyst at the rate of 30 grams/hour and 60 ml/minute respectively. After 2 hours with the reactor temperature at 550°C, the water flow was stopped and the catalyst was cooled to ambient. The steamed catalyst was treated in refluxing 1M aqueous nitric acid for one hour, filtered, and then washed with distilled water. This acid treatment procedure was repeated twice. The zeolite powder obtained was then dried and then calcined at 550°C for 12 hours in air.

Example 3Catalyst Preparation and Testing

The zeolite powders as prepared in Example 2 and in Example 1 (comparative) were pressed into tablets under 10 tonnes pressure. The tablets were broken and sieved into granules to pass 600 micron but not 250 micron sieves. 10 cc of the catalyst granules (4.2 g) were loaded into a tubular reactor with a coaxial thermocouple well and tested for the conversion of a methanol/butene feed. The results are shown in Tables 2 and 3. The terms used in these tables are defined as follows:-

WHSV	= weight hourly space velocity which is the weight of the methanol and hydrocarbon fed per weight of the catalyst per hour
Oven Temp.	= Temperature of reactor before introduction of feed.
Bed Temp.	= Temperature of reactor at time of collection of products.
HOS	= hours on stream
Feed%	= molar feed compositions

MeOH = methanol

Conversion = carbon molar conversion % of each feed

Selectivities = ((carbon molar yield of each component)/(total carbon molar conversions)) x 100

5        The data presented in Table 3 show that the comparison catalyst which had not been treated by the process according to the invention, shows high conversion at the beginning of the reaction, but that the conversion decreases rapidly. After regeneration of the catalyst by heating in air at 580°C for 12 hours, conversion is  
10    lower than with a fresh catalyst, and again, activity decreases rapidly. A further regeneration leads to a further loss in conversion.

By comparison, the data presented in Table 2 show that the catalyst treated by the process according to the invention has  
15    improved initial conversion especially after regeneration and that loss of conversion with time is very much less rapid. Regeneration is more successful in restoring the activity of the catalyst and, after 21 hours on stream, butene conversion is almost double that obtained using an untreated catalyst.

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TABLE 2

Catalyst H-Theta-1 As Prepared in Example 2

Oven Temp 400°C, WHSV 8.0 h<sup>-1</sup>, Pressure 3 bara

Feed 82% Methanol/18% 1-butene (molar)

5

10	Bed Temp	HOS	Conversion		Selectivities Based on					
	°C		MeOH	nC <sub>4</sub> =	C <sub>1</sub> /C <sub>2</sub>	C <sub>3</sub>	i-C <sub>4</sub> =	i-C <sub>5</sub> =	n-C <sub>5</sub> =	C <sub>6</sub> +
	434-424	2	46.7	84.3	0.8	5.6	5.4	27.3	11.0	44.7
	418-415	5	27.5	78.8	0.6	4.2	7.2	35.3	13.7	33.6
	414-412	7	17.1	69.1	0.4	3.0	7.2	38.6	14.5	31.2
15	Regenerated at 580°C									
	420	9.5	19.7	80.6	0.9	4.6	7.2	33.5	13.0	35.3
	414	12.5	21.6	76.1	0.5	2.7	6.9	35.4	13.2	36.8
20	411	14.5	14.0	52.6	0.6	2.8	9.1	41.3	15.2	25.7
	Regenerated at 580°C									
	426	17	35.4	78.8	1.1	4.2	7.6	33.0	14.1	33.7
25	420	19	22.0	71.0	0.8	2.8	6.9	35.2	13.3	35.5
	416	21	20.1	65.4	0.8	2.8	8.2	39.6	14.9	28.5

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TABLE 3 (Comparative Data)

Catalyst H-Theta-1 As Prepared in Example 1

Oven Temp 400°C, WHSV 8.0 h<sup>-1</sup>, Pressure 3 bara

Feed 82% Methanol/18% 1-butene (molar)

5

10	Bed Temp	HOS	Conversion Carbon Molar %		Selectivities Based on Carbon Molar Converted					
	°C		MeOH	nC <sub>4</sub> =	C <sub>1</sub> /C <sub>2</sub>	C <sub>3</sub>	i-C <sub>4</sub> =	i-C <sub>5</sub> =	n-C <sub>5</sub> =	C <sub>6</sub> +
	428-423	2	43.4	81.4	0.4	3.5	5.6	30.8	11.9	43.3
	411-409	5	25.3	68.5	0.4	2.3	7.9	41.4	15.5	28.2
	410	7	11.6	52.3	0.3	1.7	8.0	43.2	16.2	26.3
15	Regenerated at 580°C									
	424-415	8.5	22.4	71.2	0.8	2.9	7.4	38.1	14.7	31.2
	410	12.5	10.6	53.4	0.7	2.2	7.7	41.3	15.4	26.9
20	409	14.5	4.0	41.2	0.8	1.9	8.3	41.0	15.5	26.8
	Regenerated at 580°C									
	424-414	16	13.1	58.2	0.6	2.6	7.4	40.0	15.1	28.5
25	410-408	19	5.9	42.8	0.6	2.1	9.0	43.0	16.4	23.2
	410-408	21	3.0	34.3	1.0	2.1	9.6	45.2	17.5	18.3

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Example 4Catalyst Preparation

Sodium aluminate (0.74 kg, ex BDH, 40 wt%  $\text{Al}_2\text{O}_3$ , 30 wt%  $\text{Na}_2\text{O}$  and 30 wt%  $\text{H}_2\text{O}$ ) and potassium hydroxide (0.82 kg) were dissolved in  
5 de-ionised water (52.54 kg). Diethanolamine (9.70 kg) was added followed by the silica gel (Ludox AS40, 26.30 kg) over a period of 15 minutes with constant stirring to give a homogenous hydrogel of molar composition:

1.2  $\text{Na}_2\text{O}$  : 2.5  $\text{K}_2\text{O}$  : 32 DEA : 1.0  $\text{Al}_2\text{O}_3$  : 60  $\text{SiO}_2$  : 1308  $\text{H}_2\text{O}$   
10 where DEA is diethanolamine. The mixture was loaded into a 25 gallon autoclave and crystallised at  $175^\circ\text{C}$  for 25 hours. The autoclave was cooled to ambient and the content was filtered, washed with de-ionised water and dried at  $100^\circ\text{C}$ .

The powder was examined by X-ray diffraction and found to be  
15 highly crystalline Theta-1 zeolite.

Approximately 2.5 kg of the zeolite was spread in a tray to give a bed of four inches in depth and calcined in air at  $580^\circ\text{C}$  for 24 hours. The zeolite was ion exchanged by contacting with 1 equivalent/ $\text{dm}^3$  ammonium nitrate solution (1 litre/0.1 kg zeolite)  
20 and mixing at ambient temperature for 16 hours. The zeolite was filtered, washed with de-ionised water and the ion exchange treatment was repeated twice more. The last ion exchange treatment was continued for 70 hours. The washed dried ion exchanged zeolite was calcined as above at  $550^\circ\text{C}$  for 24 hours.

25 The zeolite was mixed with a commercially available silica/alumina material sold under the Trade Mark "Hymod Excelsior PKX1" and supplied by English China Clays and the mixture extruded to give extrudates whose zeolite content was 82% by weight.

Example 5Catalyst Steaming and Acid Washing  
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10 grams of the catalyst extrudates prepared in Example 4 were steamed and acid treated according to the present invention as follows:

The extrudates were placed in a tubular reactor (60 mm ID) and  
35 heated to  $550^\circ\text{C}$ . There was a large preheating zone on which water

was converted to steam before it came into contact with the catalyst. Distilled water and nitrogen were passed over the catalyst at the rate of 30 grams/hour and 60 ml/minute respectively. After 2 hours the water flow was stopped and the catalyst was cooled to ambient. The catalyst was then refluxed in 1 equivalent/litre nitric acid (10 grams of catalyst/200 ml of acid solution) for 1 hour. The extrudates were filtered, washed with distilled water and refluxed as before twice more. Finally the catalyst was calcined at 550°C for 16 hours.

10 Example 6

Catalyst Testing

The extrudates prepared in Examples 4 (Comparative) and 5 were tested for the structure isomerisation of n-butene in a feed to produce isobutene in a fixed bed tubular reactor (12 mm ID) with a co-axial thermocouple well (2 mm OD). The feed had the composition:

	<u>Component</u>	<u>wt%</u>
	isobutane	12.78
	n-butane	25.97
	t-butene-2	3.77
20	1-butene	48.90
	isobutene	0.78
	c-butene-2	7.07
	n-pentenes	0.07
	hexenes	0.60
25	octenes	0.06

The reaction pressure and temperature were 2 bars absolute and 500°C respectively. The volume of the catalyst was 5 ml and its weight was 2.02 grams. The weight of the feed in grams passed over 1 gram of catalyst per hour was fixed at 38-42. When the comparative catalyst not treated according to the invention (Example 4) was tested, after 23.5, 47.5 and 53.5 hours on stream the levels of isobutene in the total product were 16.7 wt%, 14.0 wt% and 14.3 wt% respectively. The proportions of the converted linear butenes that were converted to isobutenes (selectivity) at these times were 74.4 wt%, 78.5 wt% and 81.5 wt% respectively.

In contrast, when the catalyst according to the invention (Example 5) was tested after 24.5 and 49.5 hours on stream the levels of isobutene in the total product were 19.5 wt% and 19.7 wt% respectively. The proportions of the converted linear butenes that were converted to isobutenes (selectivity) at these times were 73.8 wt% and 83.2 wt% respectively.

#### Example 7

A batch of the hydrogen form of zeolite Theta-1 was prepared as described in Example 1 and steam and acid treated as described in Example 2. The zeolite was again pressed into tablets under 10 tonnes pressure, broken into granules and sieved to pass 600 micron but not 250 micron sieves. The granules were tested for the structural isomerisation of n-butene in the feed to produce isobutene in a fixed bed tubular reactor (12 mm ID) with a co-axial thermocouple well (2 mm OD). The feed had the composition:

<u>Component</u>	<u>wt%</u>
isobutane	11.59
n-butane	24.39
t-butene-2	7.28
1-butene	48.44
isobutene	0.81
c-butene-2	7.23
n-pentenes	0.09
hexenes	0.05
octenes	0.12

The reaction pressure and temperature were 2 bars absolute and 500°C respectively. The volume of the catalyst was 5 ml and its weight was 1.83 grams. The weight of the feed in grams passed over 1 gram of catalyst per hour was fixed at 45-47. After 77 hours on stream the catalyst was regenerated in 10-20% air in nitrogen at 580°C for 48 hours and then in air for an additional 12 hours. Nitrogen was passed over the catalyst and the temperature was reduced to 500°C. The catalyst was tested again as described above using the same feed and at the same conditions. The weight of the feed in grams passed over 1 gram of catalyst per hour was fixed at

42-44. After 24.5 and 48.0 hours on stream the levels of isobutene in the total product was 20.6 wt% and 18.2 wt% respectively. The proportions of the converted linear butenes that were converted to isobutenes (selectivity) were 72.4 wt% and 80.3 wt% respectively.

- 5 After 73 hours on stream the catalyst was regenerated as described before and testing was recommenced. After 24.0 and 48.0 hours on stream the levels of isobutene in the total product were 20.6 wt% and 18.2 wt% respectively. The proportions of the converted linear butenes that were converted to isobutenes (selectivity) were 74.1
- 10 wt% and 81.0 wt% respectively.

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## Claims:

1. A process for the conversion of a hydrocarbon feed characterised in that the feed is contacted with a zeolite catalyst to produce a product, said zeolite having a framework structure which includes a 10- or 12-member channel that is not intersected by another 10- or 12-member channel, and having been treated by a process which comprises a first step of contacting the zeolite with steam and a subsequent step of contacting the zeolite with an acid.
2. A process according to Claim 1 in which hydrocarbon feed comprises at least one olefin.
- 10 3. A process according to Claim 1 or Claim 2 in which the product comprises at least one olefin, said olefin being different to the hydrocarbon of the feed.
4. A process as claimed in any one of the preceding claims in which the zeolite is selected from the following structure types: TON, 15 MTT, ZSM-48, FER, EUO, MTW and MOR.
5. A process as claimed in Claim 4 in which the zeolite is of TON-type structure.
6. A process as claimed in any one of the preceding claims in which the zeolite is in the hydrogen form.
- 20 7. A process as claimed in any one of the preceding claims in which said first step of the zeolite treatment process is carried out at a temperature in the range of from 100 to 800°C and said second step is carried out at a temperature in the range of from 5 to 200°C.
8. A process as claimed in any one of the preceding claims in which 25 said second step of the zeolite treatment process is carried out

using a dilute mineral acid.

9. A process according to any one of the preceding claims in which a feed comprising of a C<sub>3</sub> and/or C<sub>4</sub> olefinic feed and methanol, formaldehyde and/or dimethyl ether is converted into at least one higher olefinic hydrocarbon.

10. A process according to any one of Claims 1 to 8 for the conversion of a C<sub>4</sub> to C<sub>10</sub> linear olefinic feed to branched olefins.

11. A treatment process for a zeolite which comprises a first step of contacting the zeolite with steam and a subsequent step of contacting the zeolite with an acid wherein said zeolite is selected from the structure types TON, ZSM-48, FER, EUO and MTW.

12. A treatment process according to Claim 11 in which the zeolite is of TON-type structure.

13. A treatment process according to Claim 11 or Claim 12 in which the zeolite is in the hydrogen form.

14. A treatment process according to any one of Claims 11 to 13 in which said first step is carried out at a temperature in the range of from 100 to 800°C and said second step is carried out at a temperature in the range of from 5 to 200°C.

15. A treatment process according to any one of Claims 11 to 14 in which the acid is a dilute mineral acid.

16. The use of a zeolite treated by a process which comprises a first step of contacting the zeolite with steam and a subsequent second step of contacting the zeolite with an acid, said zeolite having a framework structure which includes a 10- or 12-member channel that is not intersected by another 10- or 12-member channel, for the conversion of a hydrocarbon feed to a product comprising a different hydrocarbon.

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C07C2/86; 801J29/38		
<b>II. FIELDS SEARCHED</b> Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C07C ; 801J	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US,A,4 579 993 (EMMERSON BOWES ET AL.) 1 April 1986 cited in the application see claims 1-2,9; example ---	11,13-15
A	US,A,4 658 075 (RALPH M. DESSAU ET AL.) 14 April 1987 cited in the application see claims; examples ---	1-16
A	EP,A,0 247 802 (BP) 2 December 1987 cited in the application see claims; examples -----	1-16
<sup>10</sup> Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 28 OCTOBER 1992		Date of Mailing of this International Search Report 02. 11. 92
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer ZERVAS B.

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9201325  
SA 62476

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 28/10/92

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